Phase Transitions in Systems with Finite Number of Atoms

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Keywords: ordering, Curie temperature, magnetic phase transition, concentration phase transition, particles with a finite number of atoms.

arXiv:1201.1562v1 [cond-mat.mes-hall] 7 Jan 2012

Abstract. Properties of nanoparticles have been studied within the framework of Ising model and the method of random-field interactions: the average magnetic moment and position of critical points of the magnetic and the concentration phase transitions depending on their size. It is shown that the Curie temperature is inversely proportional to the size of the particle. Critical concentration of the ordered state decreases with increasing of size of nanoparticles until the percolation threshold of massive particles.

Introduction

Influence of surface on the magnetic properties of nanoparticles becomes substantial with decreasing of their size, if the number of atoms on the surface is comparable (or exceeds) the number of atoms inside the particle [1]. Thus the low-temperature (97 K) measurements [2,3] revealed that the specific magnetic moment $\langle\mu\rangle$ decreases with increasing of number of atoms in nanoparticles of iron, cobalt and nickel up to the values of the magnetic moment of massive sample. In contrast to nanoparticles of 3d-metals mentioned above, for rare-earth elements the magnetic moment increases with the growth of number of atoms [2,4]. It is shown [5], that the saturation magnetization of nanoparticles of α-Fe (with sizes up to 7 nm) is much smaller than in massive iron. We should note the fact, that the Curie temperature decreases with decreasing of the particle size [6].

These features of the magnetic properties of nanoparticles may be associated with a reduction (compared to the massive particles) in the number of nearest neighbors and, consequently, the weakening of the interaction between the atoms.

Model

Magnetic atoms are distributed over N^3 sites of the cubic lattice with a probability p. Thus p is the concentration of magnetic atoms and N is the total number of atoms on the edge of the cubic-shaped nanoparticle. According to [7], the distribution function for random interaction fields H on a particle located at the origin can be defined as:

$$W(H) = \int \delta\left(H - \sum_k h_k(\mathbf{r}_k, \mathbf{m}_k) \prod_k F(\mathbf{m}_k)\, \delta(\mathbf{r}_k - \mathbf{r}_{k0})\right) d\mathbf{r}_k d\mathbf{m}_k, \tag{1}$$

where $\delta(x - x_0)$ — Dirac delta function, $h_k = h_k(\mathbf{m}_k, \mathbf{r}_k)$ — field created by atoms with magnetic moments $\mathbf{m}_k$ located at coordinates $\mathbf{r}_k$, $\mathbf{r}_{k0}$ — the coordinates of lattice sites, $F(\mathbf{m}_k)$ — the distribution function for the magnetic moments, which in the approximation of Ising model for a ferromagnets can be represented as follows:

$$F(\mathbf{m}_k) = (\alpha_k \delta(\theta_k) + \beta_k \delta(\theta_k - \pi))\left((1-p)\,\delta(m_k) + p\delta(m_k - m_0)\right). \tag{2}$$

Here θ_k — the angle between $\mathbf{m}_k$ and OZ-axis, α_k and β_k — relative probabilities of the spin orientation along and against OZ-axis ($\theta_k = 0$ and $\theta_k = \pi$, respectively); m_0 — the magnetic moment of the magnetic atom. In the approximation of nearest neighbors and the direct exchange interaction between magnetic atoms, the equation (1) can be represented as:

$$W_j(H) = \sum_{n=0}^{z} p^{z-n}(1-p)^n \sum_{\nu}^{C_z^{z-n}} \sum_{l_\nu \in L(C_z^n(k_j))}^{2^n} \omega_{l_\nu} \delta(h - M_{l_\nu} J), \tag{3}$$

where k_j is a set of nearest neighbors of the magnetic atom numbered as j, $z = \dim k_j$ — its coordination number; $C_z^n(k_j)$ — sample of n atoms of the total number of z nearest neighbors of j^{th} atom; $L(\Omega)$ is a binomial set of permutations of an arbitrary set Ω with the amount of elements equal to $2^{\dim \Omega}$. Introducing the notation $\alpha_{-n} \equiv 1 - \alpha_n$ we have got $\omega_{l_j} = \prod_{(\nu=1; l_\nu \in k_j)}^{z} \alpha_{\pm l_v}$ and $M_{l_j} = \sum_{n \in k_j} \pm m_n = m_0 \sum_{n \in k_j} \pm |2\alpha_n - 1|$. Finally, J is the constant of exchange interaction.

Using the expression for the distribution function of the interaction fields (3), one can obtain equations that determine average relative magnetic moments at each lattice site:

$$\mu_j = \int \tanh\left(\frac{m_j H}{k_B T}\right) W_j(H)\, dH = \sum_{n=0}^{z} p^{z-n}(1-p)^n \sum_{\nu}^{C_z^{z-n}} \sum_{l_\nu \in L(C_z^n(k_j))}^{2^n} \omega_{l_\nu} \tanh\left(\frac{M_{l_\nu} J}{k_B T}\right). \tag{4}$$

Expression (4) allows to investigate the dependence of the magnetic moment $M = \sum_{j=1}^{N^3} \mu_j$ on the temperature T and concentration p, as well as to determine the dependence of the phase transition temperature and the percolation threshold on the number N of atoms. System of equations (4) can be solved numerically with Newton's method.

Results

Fig. 1 represents the temperature dependence of the specific (per atom) magnetic moment $\langle \mu \rangle = M/N^3$ of the particles with different number of magnetic and non-magnetic atoms. Calculations were performed for a simple cubic lattice. As expected, reducing the number of magnetic atoms leads to a reduction in the number of nearest neighbors and, consequently, to lowering the Curie temperature.

Note that the increase in Curie temperature with increasing number of magnetic atoms is described fairly well by a linear function of $1/N$ (see Fig. 2), which is consistent with experimental results [8].

Dependence of the Curie temperature on the number of atoms on the edge of cubic-shaped particle is shown on Fig. 3. Decrease in the Curie temperature is associated both with the decrease in the concentration of magnetic atoms and the weakening of the interaction (decrease in the number of nearest magnetic neighbors).

Reducing the concentration of magnetic atoms p and, consequently, the interaction between them leads to loss of ordering at a certain critical concentration p_c — point of the concentration phase transition (see Fig. 3, on the right). One can see that the curve $p_c = p_c(N)$ asymptotically tends to $p_c(N \to \infty) = 0.31$ — the well-known percolation threshold for a simple cubic lattice [10].

References

[1] S. Gubin, "Russian chemical journal," vol. XLIV (6), no. 23, 2000.

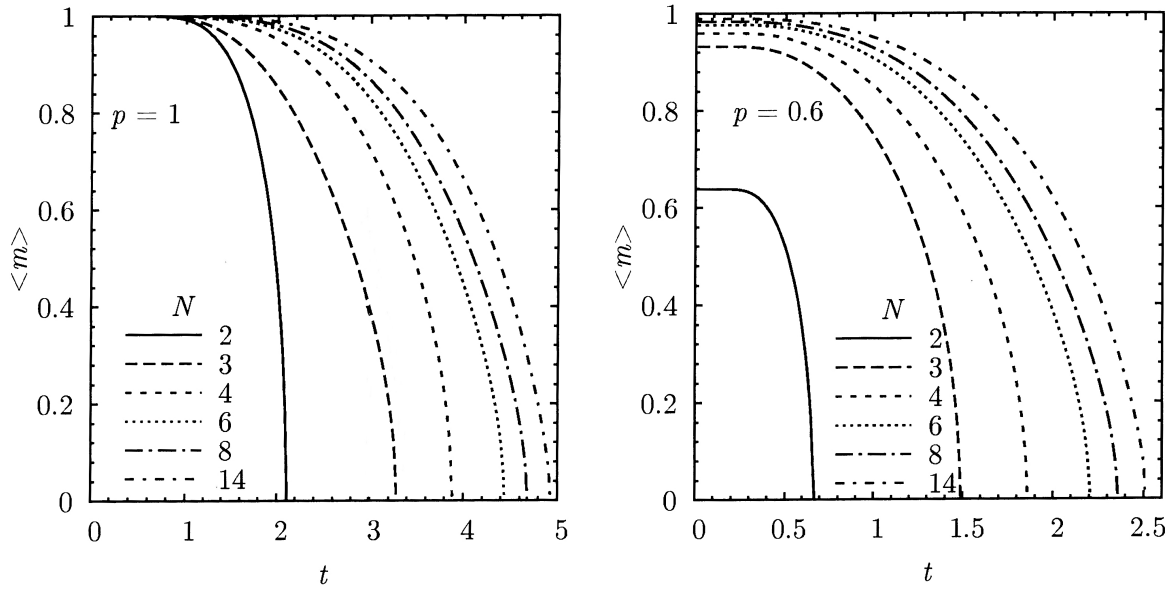

Fig. 1: The dependence of the specific magnetic moment of nanoparticles of different sizes on the reduced temperature $t = k_B T/m_0 J$ (for different concentrations p)

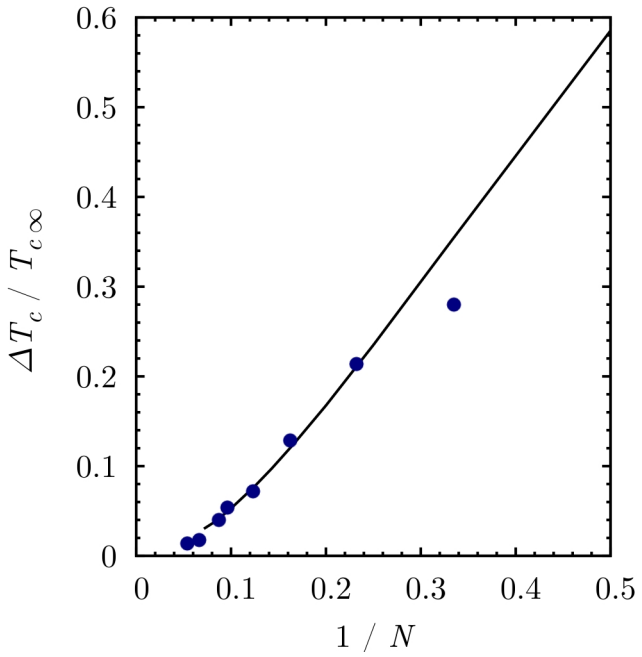

Fig. 2: Dependence of relative change in the Curie temperature on the inverse number of atoms on the edge $1/N$. Here $T_{C\infty} = T_C(N \to \infty)$ is the Curie temperature of a massive particle, and $\Delta T_C = T_{C\infty} - T_C(N)$. The dots mark the experimental results [8]. We should notice that the experimental points correspond the lattice, that differs from simple cubic. But according to our previous work [9], behaviour of the curve on this figure in such the coordinates conforms to the critical exponent λ and is independent on the type of the lattice

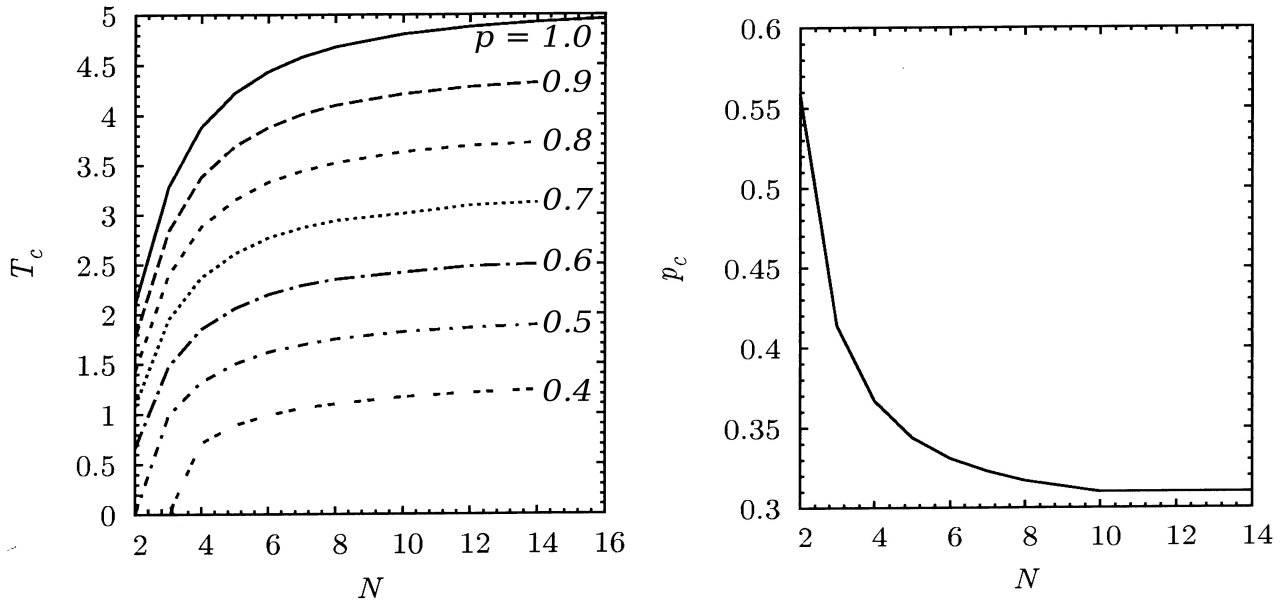

Fig. 3: Dependence of the Curie temperature (on the left) and the critical concentration (on the right) on the number N of atoms on the edge of cubic-shaped particle at different concentrations of magnetic atoms

[2] I. Billas, A. Châtelain, and W. de Heer, "Magnetism of Fe, Co and Ni clusters in molecular beams," *Journal of magnetism and magnetic materials*, vol. 168, no. 1–2, pp. 64–84, 1997.

[3] I. Billas, A. Châtelain, and W. de Heer, "Magnetism in Transition-Metal Clusters from the Atom to the Bulk," *Surface Review and Letters*, vol. 3, no. 1, pp. 429–434, 1996.

[4] P. Jena, S. Khanna, and B. Rao, eds., *Physics and chemistry of finite systems: from clusters to crystals*, vol. 1, p. 759. Amsterdam: Kluwer Academic Publishers, 1992.

[5] F. Bentivegna, J. Ferré, M. Nỳvlt, J. Jamet, D. Imhoff, M. Canva, A. Brun, P. Veillet, Š. Višňovskỳ, F. Chaput, and J. Boilot, "Magnetically textured γ-FeO nanoparticles in a silica gel matrix: Structural and magnetic properties," *Journal of applied physics*, vol. 83, p. 7776, 1998.

[6] V. Nikolaev and A. Shipilin, "The influence of breaking of exchange bonds on the curie temperature," *Physics of the Solid State*, vol. 45, pp. 1079–1080, 2003. 10.1134/1.1583793.

[7] V. Belokon and K. Nefedev, "Distribution function for random interaction fields in disordered magnets: Spin and macrospin glass," *Journal of Experimental and Theoretical Physics*, vol. 93, pp. 136–142, 2001. 10.1134/1.1391530.

[8] B. Sadeh, M. Doi, T. Shimizu, and M. Matsui, "Dependence of the Curie Temperature on the Diameter of Fe_3O_4 Ultra-Fine Particles," *Journal of the Magnetics Society of Japan*, vol. 24, no. 4/2, pp. 511–514, 2000.

[9] L. Afremov and Y. Kirienko, "Magnetic phase transitions in ultrathin films of different crystal structures," *Advanced Materials Research*, vol. 378, pp. 589–592, 2012.

[10] A. Efros, *Physics and geometry of disorder: Percolation theory*. Mir Publishers, 1986.